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13. ABSTRACT (Maximum 200 words)

The fire suppression effectiveness of aqueous solutions is studied using an opposed-jet diffusion flame burner with a droplet/particle seeding system designed to minimize loading uncertainties. An aqueous solution is sprayed into the oxidant stream in a heated chamber. The liquid evaporates, leaving residual solid particles in the case of solid solutes. SEM imaging of residual particles indicates a mean diameter of approximately 0.5 microns. Extinction measurements are presented for a variety of phosphorus-containing compounds as well as NaCl and sodium phosphate, with different loadings, solution concentrations, and oxidants. Flame calculations with two detailed phosphorus combustion mechanisms are also performed for some cases, neglecting all particle physical effects. Experiments indicated that all additives containing phosphorus had roughly the same effect on flame suppression, per mole phosphorus added. Additives producing residual particles were somewhat more effective than those that evaporated completely, suggesting a moderate enhancement of fire suppression due to particle physical effects. However, this result is also consistent with chemical differences between additives. Synergy between water and chemical suppressants was predicted computationally but not observed experimentally. Computations underpredicted flame suppression effectiveness by at least a factor of four.

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Figure 6. Comparison of normalized global extinction strain rate for 1.6% NaCl, OPA, DMMP and neat DMMP introduced into a flame using regular air (reg) or 21% O₂, 53% N₂ and 26% Ar (hot) as oxidant.

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(1) Statement of the problem studied

The current study explores the flame suppression effectiveness of aqueous solutions, focusing on phosphorus-containing solutes. This research contributes to the search for a replacement for CF_3Br , a highly effective fire suppressant that has been banned because of its effects on the ozone layer. In particular, the study investigates several issues relevant to the use of chemically enhanced water mists for fire suppression. A burner seeding system has been designed to minimize loading uncertainties associated with particle- and droplet-phase flame additives. With this apparatus, information is obtained on the likely magnitude of physical effects of particles on flame suppression, and on the extent of synergy between the chemical agent and the water. In addition, extinction measurements are presented for a variety of candidate fire suppressants including NaCl and sodium phosphate as well as several phosphorus-containing compounds.

(2) Summary of the most important results

a) Burner Characterization

Experiments and calculations were performed to characterize the operation of the burner with particle-phase suppressants. The seeding apparatus consisted of a high-efficiency nebulizer (HEN) that sprayed droplets of flame suppressant into a heated chamber, through which the air stream for the burner flowed. The air stream, bearing the suppressant, traveled down a long burner tube to the flame. When a liquid suppressant was sprayed, evaporation was complete well before the flame. When an aqueous solution with a solid-phase solute was sprayed, residual solid particles remained from the evaporation process and entered the flame. A major issue in studies of particles as flame suppressants is the accurate accounting for the delivery of suppressant to the flame. Especially when particles are large, incomplete particle vaporization in the flame, and deviations of particle trajectories from gas streamlines, can lead to large uncertainties in the amount of suppressant delivered to the gas phase in the flame. We designed the burner and atomization system to minimize these sources of uncertainty, and performed measurements showing that particles were indeed small enough to behave as desired.

One major concern was with the particles' ability to travel with the gas flow in the opposed-jet diffusion flame. Temperature and velocity fields obtained from Chemkin flame calculations (Lutz et al., 1996) were used to estimate how well particles followed the gas flow. It was concluded that as long as the particles are small (less than $\sim 6 \mu\text{m}$), they closely follow the gas streamlines in the diverging flow of an opposed-jet burner. Gravity is negligible for all particle sizes considered. Thermophoresis perturbs the flow of the particles $< 1 \mu\text{m}$, but over the lifetime of these particles the magnitude of the perturbation is relatively insignificant, compared to the size of the flame. Thus, the particles are expected to follow the gas streamlines, and information on the gas velocities and temperature profiles can be used to describe the particles.

Two methods were used to determine the size distribution of residual particles. At first, estimates were based on the initial droplet size distribution, as measured by phase Doppler particle anemometry. Residual particle sizes were estimated by assuming that each droplet evaporates to form a single spherical particle with density equal to that of

the pure solid solute. This estimate indicates a particle Sauter mean particle diameter of 3 μm , a median particle diameter of 2 μm , and a maximum particle diameter of 8 μm , under typical operating conditions. (Note that these particles are too small and irregularly shaped to be measured accurately with PDPA, which has an uncertainty of 2 μm , and which processes data on the assumption that particles and droplets are spherical.) Measured droplet size distributions varied only slightly with flowrate, solution concentration, and other operating parameters, as can be seen in Fig. 1, and so the residual particle sizes listed above are representative of a range of operating conditions and additives. The second source of information on particle sizes was extractive sampling, which was performed only for aqueous solutions of NaCl. Particles were collected on a grid inserted into the flow in the absence of a flame, and then the grid was examined with a scanning electron microscope (SEM). A representative SEM image of NaCl particles is shown in Fig. 2. This method resulted in much smaller particles: the median diameter was 0.25 μm , and the particle diameter corresponding to the mean volume was 0.8 μm . As direct measurement yielded smaller particles than were inferred from droplet size measurements, it was concluded that fragmentation of droplets and/or particles occurs downstream of the droplet size measurement location. In any case, the residual particles are clearly small enough to travel with the flow and to evaporate completely in the flame.

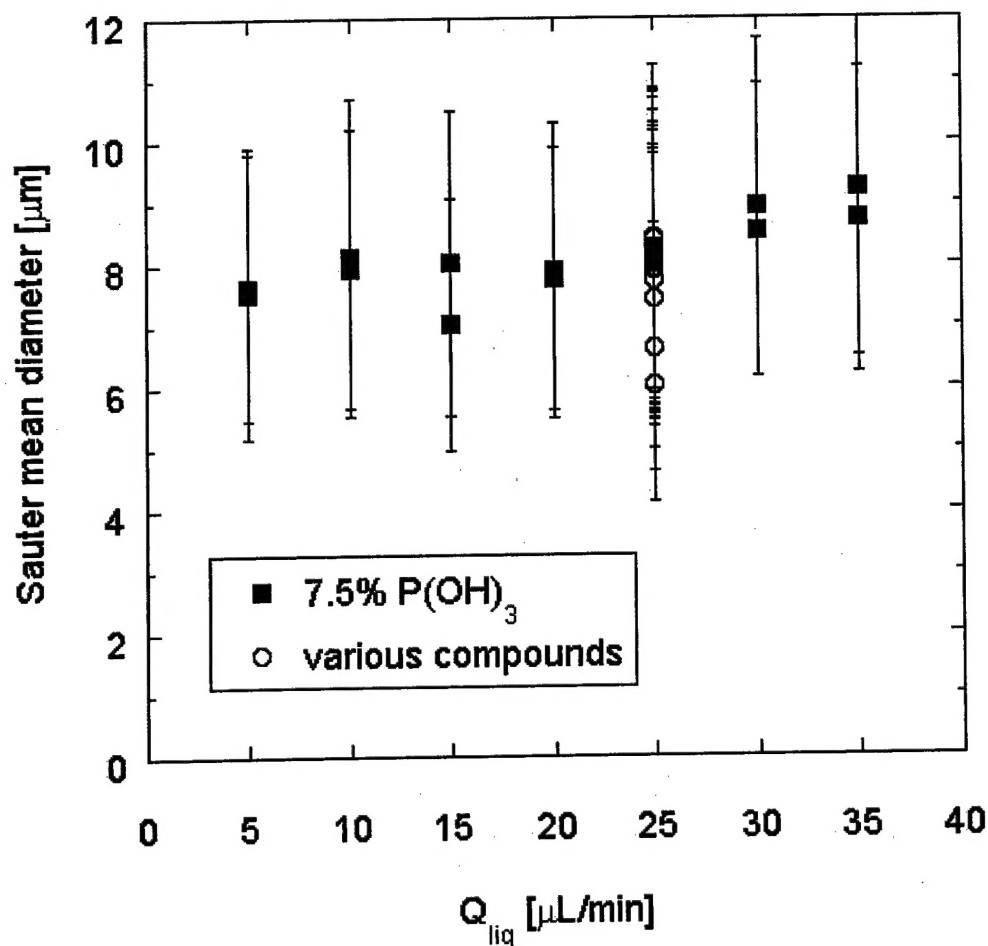


Figure 1. PDPA-measured Sauter mean diameter, 1.3 cm downstream of HEN exit, as a function of liquid flow rate. Under conditions in this paper for the 7.5% phosphorous acid solution, 25 μL/min corresponds to a total loading of 1.49%. The various compounds tested were: 7.5% phosphorous acid, 1.6% orthophosphoric acid, 7.5% phosphonic acid, 7.5% methylphosphonic acid, neat DMMP, 4.3% DMMP, and neat H₂O. All concentrations are molar based in an aqueous solution. Error bars represent one standard deviation in the diameter measurement of 2000 droplets.

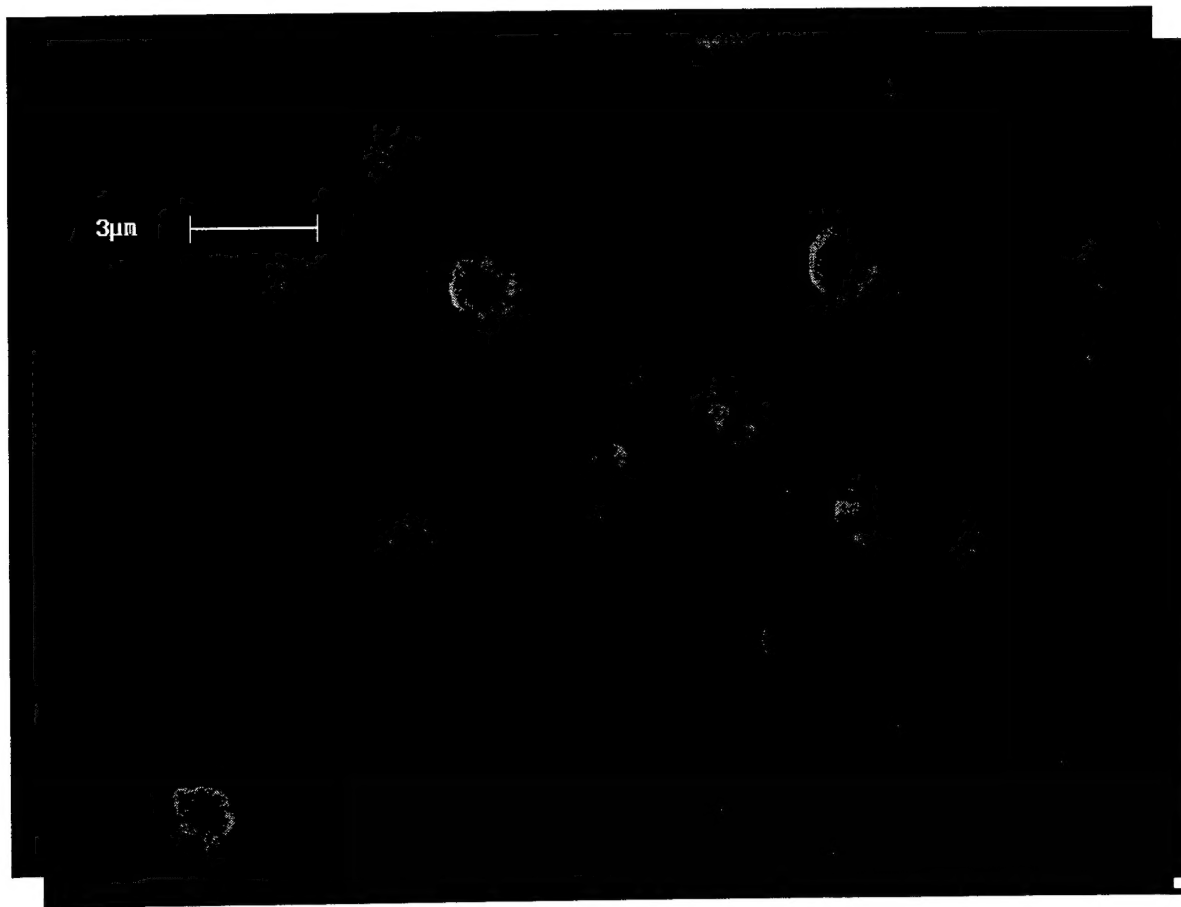


Figure 2. Sample SEM of NaCl particles collected under non-combustion conditions.

b) Effectiveness of Different Compounds, and Particle Effects on Suppression

Extinction measurements were performed in flames of methane versus air doped with several aqueous solutions and neat fire suppressant compounds. A complete list of the compounds tested is given in Table 1, with abbreviations. Extinction measurements were used for three purposes: (1) to provide information about the relative effectiveness of different flame suppressants (2) to estimate the importance of particle physical effects on flame suppression, and (3) to examine the temperature dependence of suppressant effectiveness and the synergy between water and chemical flame suppressants. Items (1) and (2) are described in the current section, while item (3) is discussed in section c) below. Additional inconclusive experiments on the effect of particle size are summarized in section (d) below.

Extinction measurements were performed various different fixed suppressant loadings, and extinction was achieved at each loading by increasing strain rate. For most suppressants, extinction strain rate was determined for a range of additive loadings. In all cases, the suppressant was introduced on the oxidant side of the flame. Figure 3 shows a representative set of results for dimethyl methylphosphonate (DMMP) and water. As can be seen in the figure, the strain rate at extinction decreases linearly as suppressant loading increases. This behavior was observed for all compounds tested over the range of loadings examined here. A convenient measure of suppressant efficacy is the absolute value of the slope of the extinction strain rate vs. suppressant loading line, referred to hereafter as the suppressant effectiveness. Clearly, DMMP, a chemically active flame suppressant, has a much higher effectiveness than water, which acts primarily as by lowering the temperature and diluting the reactant mixture. (For reference, literature on CF₃Br (Trees et al., 1995; Papas et al., 1997) indicates an effectiveness approximately one half to one third that of DMMP.) For DMMP and water, "liquid-phase" results were obtained when the suppressant was introduced through the HEN, as a spray of liquid droplets. The good agreement between those obtained earlier, with vaporized DMMP and water, confirms that the spray vaporizes completely and with minimal losses before entering the flame.

Figure 4 shows extinction strain rate vs. additive loading for various different suppressants. To facilitate comparisons among different aqueous solutions, we chose to present results as a function of phosphorus loading rather than as a function of the loading of the entire suppressant mixture (including water). Note that results have been corrected for measured losses, in the case of solutions leaving solid residues upon evaporation. In Fig. 4, aqueous solutions of phosphorus-containing compounds have higher effectiveness (per mole phosphorus) than neat phosphorus-containing compounds, because of the contribution of the water to flame suppression. Results from Figures 3 and 4 are summarized in Table 2 along with extinction results obtained with different solution concentrations, and different additives (including sodium-containing compounds). In the table, the slope of the extinction strain rate vs. additive loading curve is presented. Corrected slopes have been adjusted for the effect of the heating value of the additive, as appropriate (MacDonald et al., 1997).

Experimental results indicate a significant reduction in global extinction strain rate with the addition of pure water vapor (10% reduction at 1.5% molar loading), in good agreement with extinction calculations and with other researchers' calculations (Lazzarini et al., 2000). With the addition of a small amount (1.6% molar) of phosphorus- or sodium-containing compound in water solution, this reduction approximately doubles. Phosphorus compounds are highly effective fire suppressants, and surprisingly NaCl is found to be 13% more effective than orthophosphoric acid in suppressing a flame. These results support, and expand upon, other researchers' data suggesting the use of water as a means of delivering a chemically active, condensed-phase agent to an actual fire.

Experimental comparisons among several different PCCs, introduced in the gas and liquid phases, show that the form of the parent compound is relatively unimportant in suppression effectiveness. Differences in effectiveness between solutions with solid- or liquid-phase solutes can give an estimate of the effect of the particle in flame suppression. The suppression effectiveness of PCC solutions that produce the residual particles are all at least 20% more effective than the DMMP solution, which does not produce particles. This difference, which is much larger than the experimental uncertainty, could be due to physical effects of the residual particles, for example enhanced radiative heat transfer away from the flame. If so, then the physical particle effect is somewhat smaller than the chemical effect of the additive. It is possible, however, that differences in chemical effectiveness among the different phosphorus compounds may account for the observed differences.

Two types of chemical kinetic calculations, using the Chemkin OPPDIF code (Lutz et al., 1996), were performed to elucidate experimental results. Phosphorus combustion mechanisms developed by Glaude and coworkers (Glaude et al., 2000) and Babushok and coworkers (Babushok, 2001; Wainner et al., 2000) were used. In these calculations, the phosphorus additives were treated as gas-phase compounds, and no droplet or particle effects were modeled. First, OPPDIF was used to determine levels of flame radicals for a representative flame condition, with and without phosphorus additives; these results are discussed in section c) below. Then for more direct comparison with experiment, extinction calculations were performed. Calculated strain rates at extinction are presented in Table 3.

In the extinction calculations, both mechanisms predict much lower flame suppression effectiveness than was observed experimentally. One mechanism (Wainner et al., 2000) indicates that the addition of 250 ppm of DMMP had no significant effect on the strain rate at extinction. The other mechanism (Glaude et al., 2000) shows a reduction in extinction strain rate of about 1.5%, while 7% was observed experimentally. These severe underpredictions were seen for all the compounds for which calculations could be performed. However, the ranking of effectiveness, (orthophosphoric acid > $P(OH)_3$ > DMMP) is the same as observed experimentally, and the fractional change of effectiveness from compound to compound is comparable to that observed experimentally. These observations suggest that differences in chemical effectiveness, rather than particle physical effects, may account for observed differences between phosphorus acid compounds and DMMP. Clearly, improvements to the phosphorus combustion mechanisms would help clarify this point.

Table 1. List of compounds used in experiments. Given are the name of the compound, along with abbreviations used in the text, the form in which the compound was introduced, where all solutions made were aqueous, the CAS number and the molecular formula.

Compound	Form	CAS number	Molecular formula
Distilled water	neat liquid, vapor solution	7732-18-5 7664-38-2	H ₂ O P(=O)(OH) ₃
Orthophosphoric acid (OPA)	solution	10294-56-1	P(OH) ₃
Phosphorous acid	solution	13598-36-2	P(=O)(H)(OH) ₂
Phosphonic acid	solution	993-13-5	P(=O)(CH ₃)(OH) ₂
Methylphosphonic acid (MPA)	solution	7722-76-1	(NH ₄)H ₂ PO ₄
Monoammonium phosphate (MAP)	neat liquid, vapor, solution	756-79-6	P(=O)(CH ₃)(OCH ₃) ₂
Dimethyl methylphosphonate (DMMP)	neat vapor	868-85-9	P(=O)(OCH ₃) ₃
Dimethyl phosphate	neat vapor	683-08-9	P(=O)(CH ₃)(OCH ₂ CH ₃)
Diethyl methylphosphonate (DEMP)	solution	7647-14-5	NaCl
Sodium chloride	solution	7558-80-7	(Na)H ₂ PO ₄
Sodium phosphate			

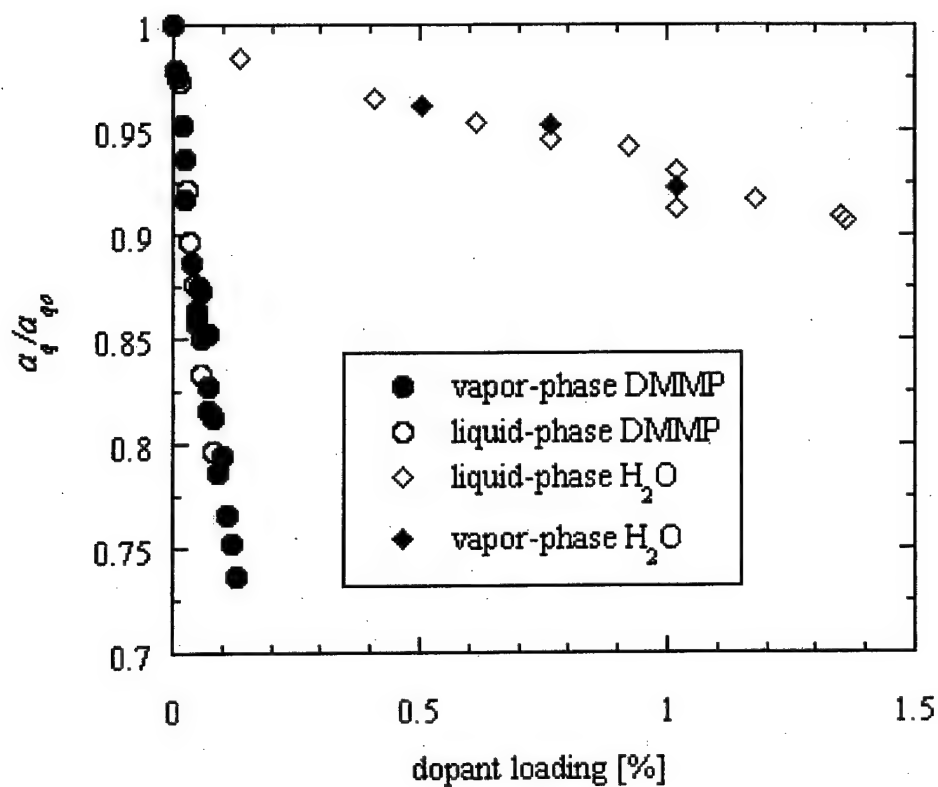


Figure 3. Normalized global extinction strain rate of neat DMMP and H₂O, as a function of dopant loading. The dopant was introduced either as a spray via the HEN (liquid phase) or in the vapor phase upstream of the oxidizer flow tube. Loadings are given as the mole fraction of dopant in the oxidizer stream assuming complete vaporization.

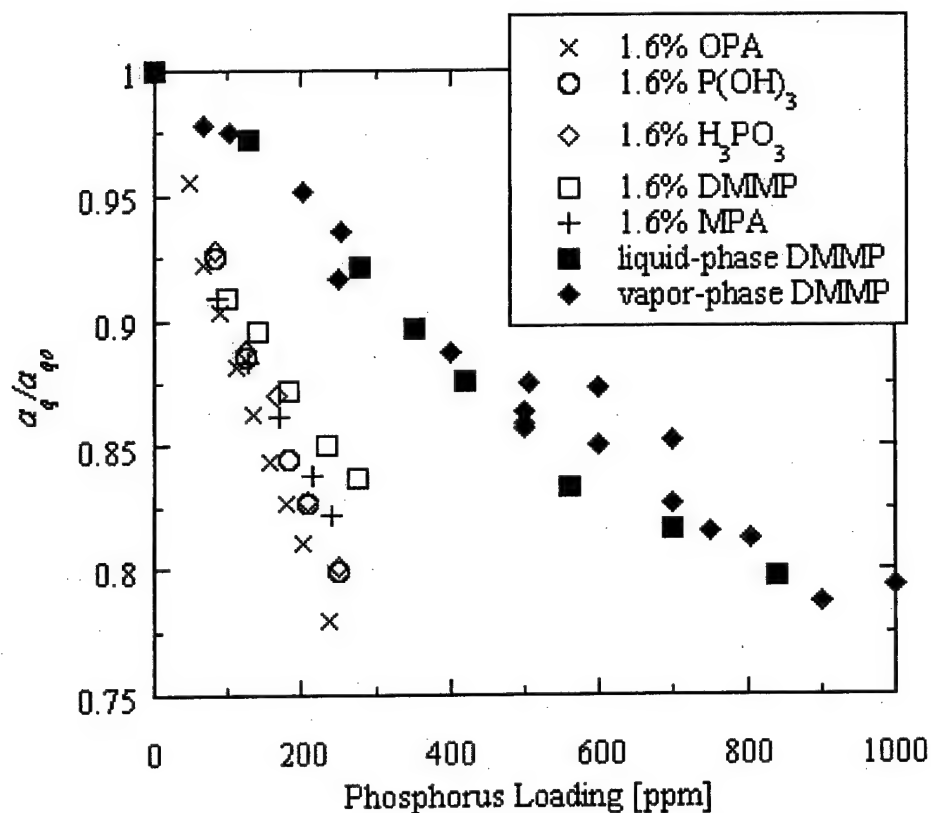


Figure 4. Comparison of normalized global extinction strain rate as a function of phosphorus loading for several different phosphorus-containing compounds. DMMP was introduced in the vapor phase upstream of the chamber and in the liquid-phase via the HEN. All other compounds, including 1.6% (molar) aqueous solutions of DMMP, orthophosphoric acid, phosphorous acid, phosphonic acid, and methylphosphonic acid, are introduced in the liquid phase via the HEN. The phosphorus loadings for the acid solutions have been corrected for wall losses.

Table 2. Global extinction strain rate reduction by the compounds tested. The slope is of normalized extinction strain rate vs. agent loading. The uncertainty in the slope is 2.5%. The units for the slopes are inverse loading, where the loading for the solutions is that of the solute, calculated by assuming it has completely evaporated. Corrected slope is the slope corrected for heating value of the agent.

Compound (neat compound)	Slope	Corrected slope
DMMP	223	267
TMP	269	311
DMP	247	278
DEMP	204	255
H ₂ O	688	
Compound (1.6% aqueous solution)		
Orthophosphoric acid (OPA)	997	996
Phosphorous acid	835	840
Phosphonic acid	814	818
Methylphosphonic acid	792	808
Dimethylmethyl phosphonate (DMMP)	654	697
NaCl	1130	
NaH ₂ PO ₄	892	
Compound (other concentrations)		
0.8% MAP	1296	
6.4% OPA	948	947
3.3% NaCl	1181	

Table 3. Summary of extinction strain rates calculated. The effect of PCCs was found using either Glaude's or Babushok's PCC mechanism. All dopants are introduced with 250ppm of PCC and/or 1.54% H₂O. In this table, all calculations were done using air as oxidant.

Dopant	Extinction strain rate [s ⁻¹]
Undoped	604.2
DMMP (Glaude)	595.3
DMMP (Babushok)	603.1
OPA (Glaude)	585.4
OPA (Babushok)	603.1
P(OH) ₃ (Glaude)	590.1
H ₂ O	534.7
DMMP + H ₂ O (Glaude)	524.8
DMMP + H ₂ O (Babushok)	533.6
OPA + H ₂ O (Glaude)	519.1
OPA + H ₂ O (Babushok)	533.6
P(OH) ₃ + H ₂ O (Glaude)	524.8

c) Temperature Dependence and Synergy.

Some experiments and calculations indicate that the effectiveness of chemical agents increases with decreasing temperatures (Lott et al., 1996, MacDonald et al., 2001, Saso et al., 1999a, 1999b). These observations suggest that there should be advantages to combining a chemically active suppressant with a physical suppressant, such as water, that lowers the flame temperature. It is also possible that water may enhance the effectiveness of phosphorus-based flame suppression through enhanced 3rd body effectiveness in key reactions involving phosphorus-containing radicals. We performed experiments and calculations to measure synergy directly, and also to determine the temperature dependence of flame suppression effectiveness.

To test the synergy of a phosphorus-containing additive with H₂O, the extinction results of DMMP and H₂O are used. Referring back to Figs. 3 and 4, the results for the 1.6% solution of DMMP can be used to assess whether DMMP and water have additive or synergistic effects. Linear regressions of the data in Fig. 3 give values of the slopes of the normalized extinction strain rate vs. mole fraction for neat DMMP and H₂O. If DMMP and H₂O acted synergistically, a weighted average of their individual effectivenesses would underpredict the measured effectiveness. However, a weighted average of these two numbers yields a predicted "effectiveness" of a 1.6% solution of DMMP in water to be 4% *higher* than the measured effectiveness of the solution. Thus, additivity of effectiveness is valid under the conditions of the current experiment, and synergy is not observed. Note that the temperature change induced by the H₂O is small (about 20 K), making synergy hard to observe experimentally.

Computationally, it is simple to separate the effects of the water and the phosphorus-containing compound. To do this, 250 ppm of a phosphorus-containing compound was added to the flame with and without 1.54% of H₂O. Calculations were performed with H₂O and the phosphorus compound added separately and together. The change in flame radical (OH, H, and O) populations between undoped and doped flames is determined for each case. Maximum radical levels are also shown in Fig. 5a (Babushok) and 5b (Glaude). The calculations indicate that the PCC and H₂O effects are additive, such that the sum of the differences in radical levels is nearly equal to that obtained when both dopants are introduced together. Thus, based on radical population, there is no indication of a synergy effect between the two compounds.

Extinction calculations, using Glaude's mechanism, indicate some synergy between phosphorus compounds and H₂O. Without H₂O, DMMP and P(OH)₃ reduced the extinction strain rate by 1.5% and 2.3% respectively, while for OPA the reduction was 3.2%. With the addition of 1.54% H₂O, a linear combination of effectiveness would result in a reduction of 13%, 13.8% and 14.7% for DMMP, P(OH)₃ and OPA, respectively. In fact, this reduction increased to 14.7% for DMMP and P(OH)₃, and to 14.8% for OPA. This increased suppression with H₂O is evidence of synergy.

To investigate the temperature-dependence of phosphorus flame suppression effectiveness directly, extinction measurements and calculations were performed using a different oxidant. This oxidant, composed of 21% O₂, 53% N₂ and 26% Ar (molar), has the same O₂ and inert mole fractions as regular air, but produces a 92 K higher adiabatic flame temperature for methane combustion.

In these experiments, despite the larger change in temperature, there is very little difference in normalized extinction strain rate as a function of loading between the two oxidants. Three additives were tested: 1.6% molar solutions of NaCl, OPA or DMMP were introduced, with results shown in Fig. 6. Neat DMMP is slightly less effective in the higher temperature flame, as expected. For the regular air flame, $a_q/a_{q0} = 0.82$, compared to 0.85 for the hotter flame. This difference, however, is not much larger than the standard deviation in the scatter of the data ($\pm 1\%$), which indicates that the difference is almost negligible. For the other compounds, the difference in effectiveness is negligible.

Extinction calculations were also performed with the hotter flame to help elucidate the temperature effect. The effectiveness of DMMP and OPA in the hotter flame was found using Glaude's mechanism, the results of which were given in Table 4. From these calculations, the reduction in normalized global extinction strain rate by DMMP decreased from 1.5% to 1.0% from the cooler to hotter flame. The choice of oxidant changed OPA's effectiveness by a similar percentage, reducing the reduction in normalized global extinction strain rate from 3.2% to 2.1%. The extinction calculations indicate that the dopants are less effective at higher temperatures, an effect seen slightly with the neat DMMP. When water is also introduced with the PCC in the hotter flame, the change in the reduction is slightly less. Normalizing the extinction strain rate to the H₂O-only doped value results in a reduction of 1.2% for DMMP and 2.4% for OPA. This gives evidence that the third-body effect of H₂O is important in increasing suppression by PCCs.

To summarize, synergy and temperature dependence of effectiveness were not observed experimentally, except for a slight decrease in the effectiveness of neat DMMP in the hotter flame. However, computational results indicate a synergistic interaction for the PCCs, in part due to the third-body efficiency of H₂O, and also in part due to the temperature effect. One possible explanation to why synergy was observed computationally for the PCCs, but not experimentally, is that experimentally, there may be increased particle radiation at higher flame temperatures; an effect that is not included in the computational model. This increase in heat transfer due to radiation could be offsetting some of the change in adiabatic flame temperature.

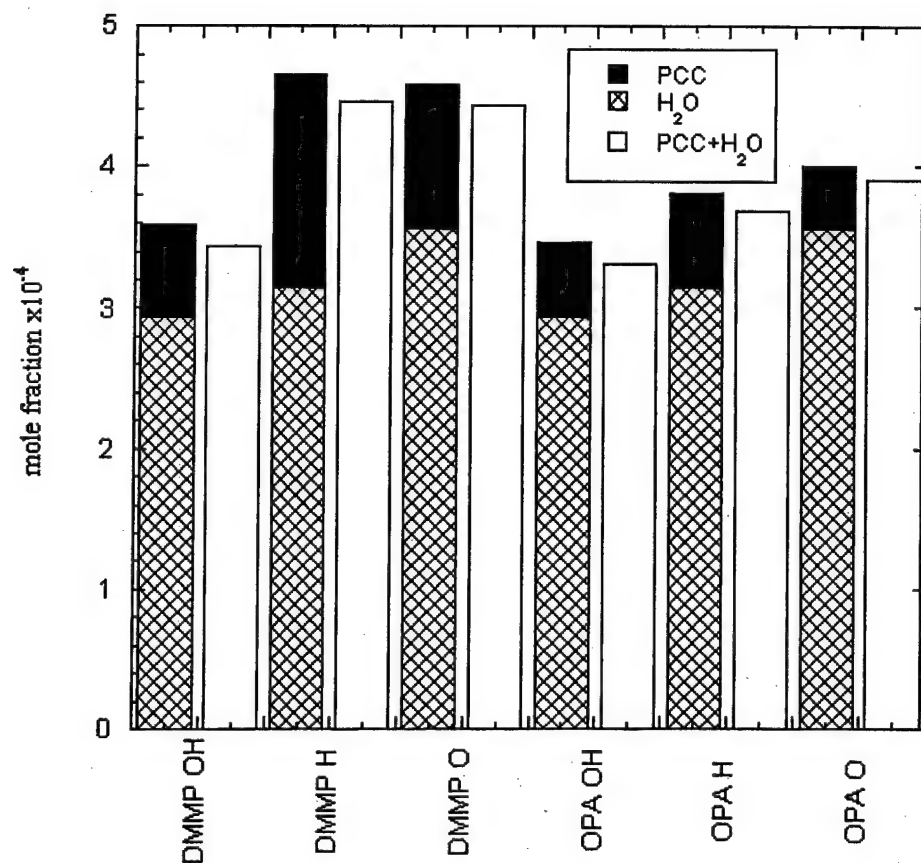


Figure 5a. . Change from undoped levels of key flame radicals, OH, H and O due to the introduction of DMMP or OPA, as calculated by Babushok's mechanism (Wainner et al., 2000). The stacked bars (hatched and solid black) are radical levels produced by either the PCC or H_2O introduced separately, while the clear bar represents radical levels when the two dopants are introduced together.

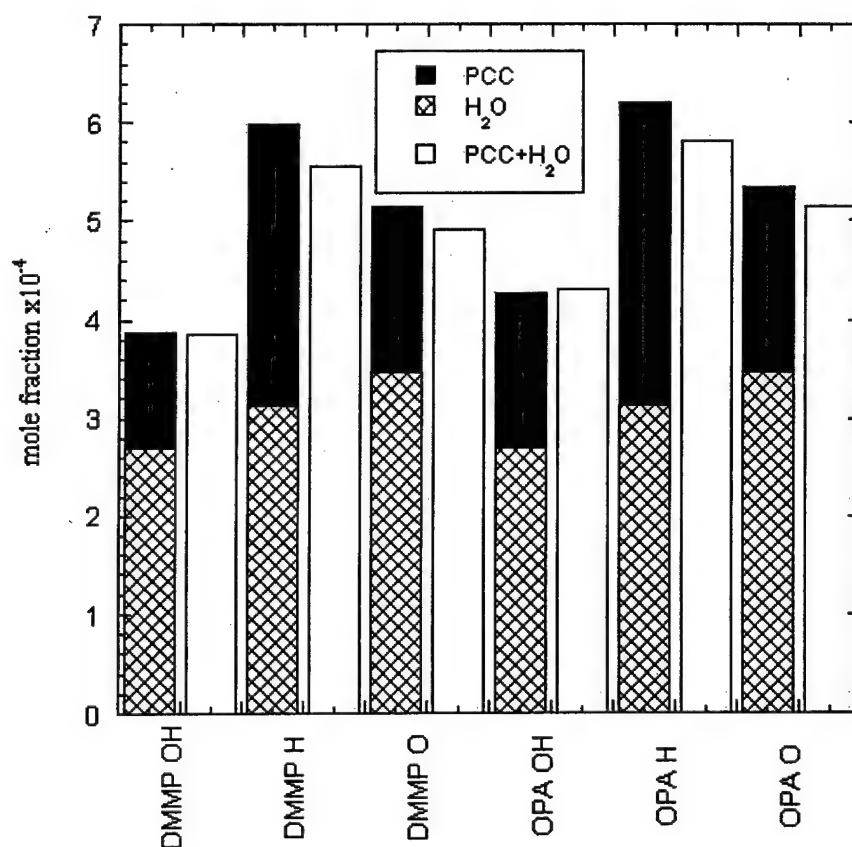


Figure 5b. Change from undoped levels of key flame radicals, OH, H and O due to the introduction of DMMP or OPA, as calculated by Glaude's mechanism (Glaude et al., 2000). The stacked bars (hatched and solid black) are radical levels produced by either the PCC or H_2O introduced separately, while the clear bar represents radical levels when the two dopants are introduced together.

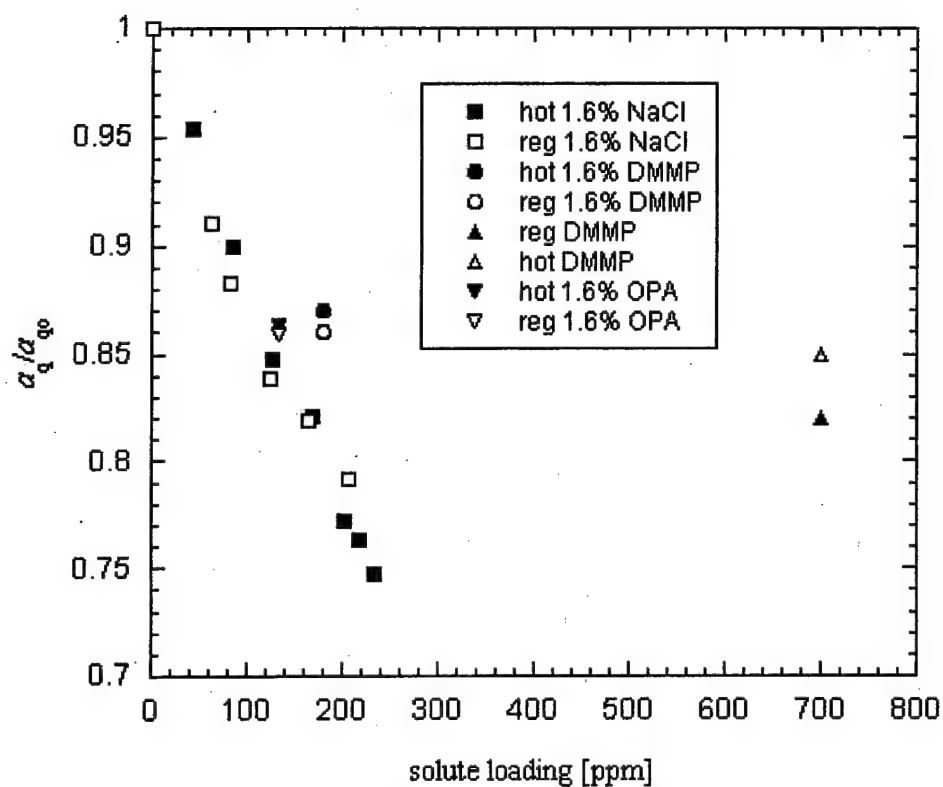


Figure 6. Comparison of normalized global extinction strain rate for 1.6% NaCl, OPA, DMMP and neat DMMP introduced into a flame using regular air (reg) or 21% O₂, 53% N₂ and 26% Ar (hot) as oxidant. The flame with the O₂/N₂/Ar mixture has an adiabatic flame temperature 92 K higher than that with regular air.

Table 4. Extinction strain rates calculated with the dopant introduced into a flame using 21% O₂, 53% N₂ 26% Ar as oxidant. Glaude's mechanism was used. All dopants are introduced with 250ppm of PCC and/or 1.54% H₂O.

Dopant	Extinction strain rate [s ⁻¹]
Undoped	977.4
H ₂ O	882.8
DMMP	967.1
OPA	956.5
DMMP + H ₂ O	872.7
OPA + H ₂ O	861.4

d) Residual Particle Size.

One physical effect that may impact the overall suppression is the size of the residual particles. To investigate this effect, extinction measurements were performed with different concentrations of solutions, but with the same total loading of both the solute and water delivered for both cases. If each droplet evaporates to form a single residual particle, different solute concentrations will yield different residual particle sizes with the same total loading. Extinction measurements were performed with higher concentration solutions of OPA (6.4%) and NaCl (3.3%) for comparison to the 1.6% solutions. The expected mean particle diameters are 3 μm and 4.5 μm for 1.6% and 6.4% OPA solutions, respectively, and 2.3 μm and 2.9 μm for 1.6% and 3.3% NaCl solutions, respectively.

The results for the difference in suppression effectiveness were given in Fig. 7. As can be seen, there is only a slight difference between the effectiveness of the two concentrations of the given compound. Based on the slopes, the two NaCl solutions differ by about 4.4%, while the OPA solutions differ by 5.0%. This spread is within the uncertainty of $\pm 2.5\%$, and the direction of change of effectiveness with expected particle size is not consistent for NaCl and OPA. If estimates of particle size described above are correct, this result indicates that the size of particles has a negligible effect on flame suppression under these conditions.

In fact, there is strong evidence that the assumption of each droplet forming a single particle is not correct. As mentioned in a) above, measured residual particle sizes were measured for NaCl, and were found to be much smaller than predicted. Figure 8 gives stacked histograms of the particle diameter for the two NaCl concentrations, as measured by SEM imaging of deposited particles. Note that the actual mean particle diameter is $\sim 0.55 \mu\text{m}$, and the difference in particle size between the two solutions is negligible. In fact, the mean particle diameter for the 3.3% solution is 0.54 μm , less than the mean of 0.56 μm obtained from the 1.6% solution. It appears that NaCl droplets or residual particles fragment before reaching the flame, and that this experiment was unsuccessful in achieving significantly different droplet size distributions. Thus no conclusions can be drawn about the effect of particle size on flame suppression effectiveness from the experiments reported here.

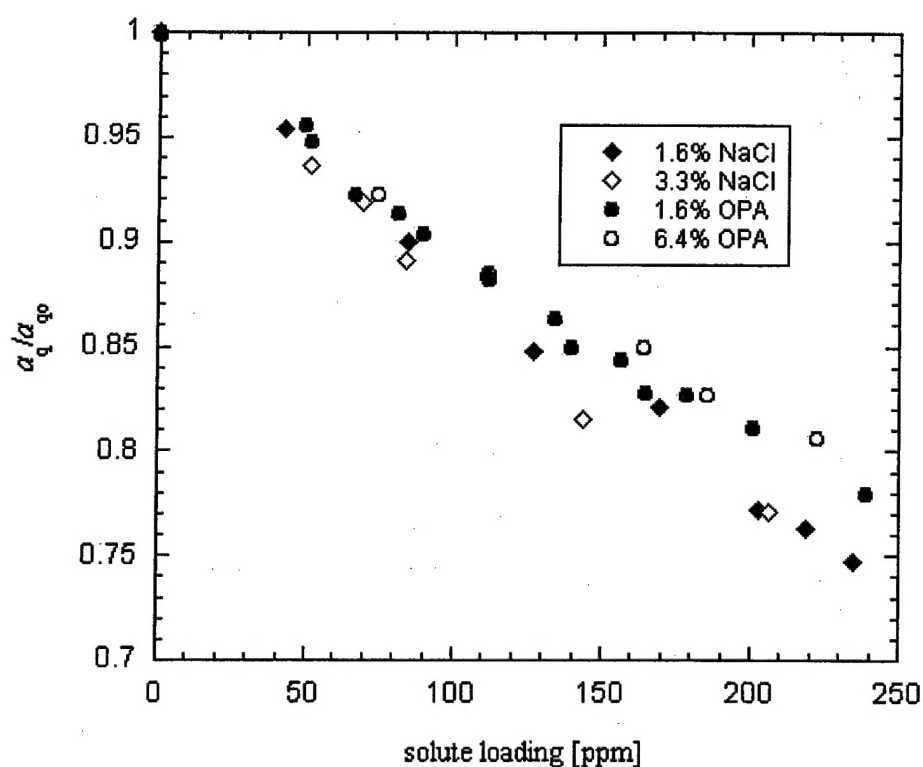


Figure 7. Normalized global extinction strain rate as a function of solute loading for two concentrations each of NaCl and OPA. The water loading for both concentrations was matched for a given solute loading by adding additional H_2O upstream of the HEN for the higher concentration solutions.

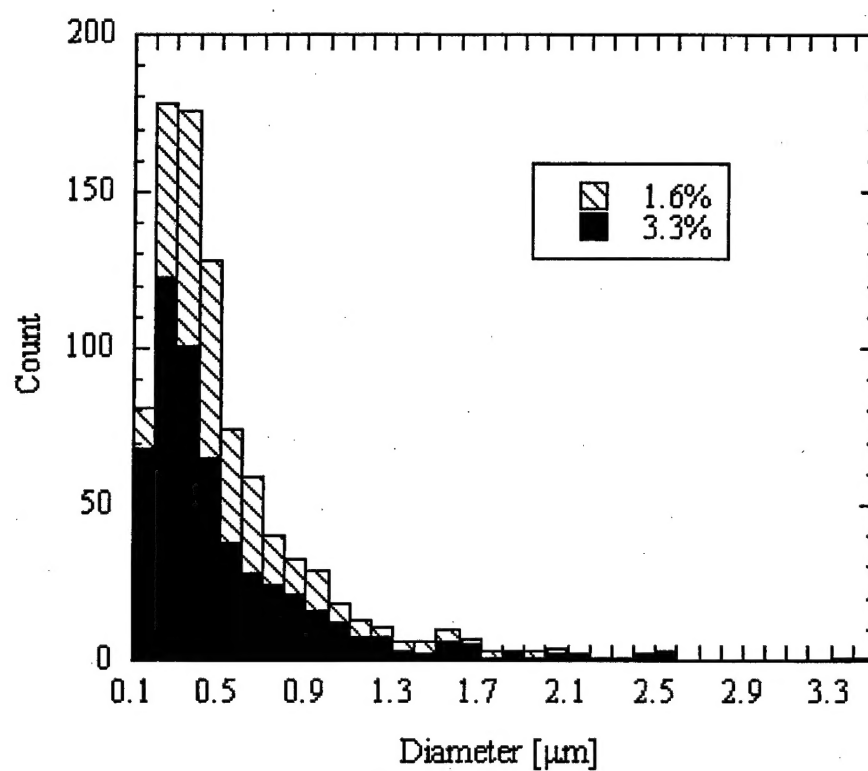


Figure 8. Stacked histograms of particle diameters deposited on grid for two concentration of NaCl solutions. The mean diameter for the 1.6% solution is 0.56 μm , and 0.54 μm for the 3.3% solution

(3) Listing of all publications and technical reports supported under this grant or contract. Provide the list with the following breakout, and in standard format showing authors, title, journal, issue, and date.

(a) Papers published in peer-reviewed journals. none.

(b) Papers published in non-peer-reviewed journals or in conference proceedings. none.

(c) Papers presented at meetings, but not published in conference proceedings none.

(d) Manuscripts submitted, but not published:

Submitted for publication in Combustion and Flame, 5/2001: T.M. Jayaweera, E.M. Fisher, and James W. Fleming, "Flame Suppression by Sprays of Aqueous Solutions Containing Phosphorus." Note: ARO sponsorship was not acknowledged in the original submission of the manuscript, which occurred shortly before the start of the current contract. We intend to acknowledge ARO sponsorship in our revised manuscript, responding to reviewers' comments, to be submitted ~4/1/02, as new material obtained during the present contract will be included in the revision.

(e) Technical reports submitted to ARO. none.

(4) Participating scientific personnel:

Elizabeth M. Fisher, Associate Professor, Mechanical and Aerospace Engineering.
Tina M. Jayaweera, Graduate Research Assistant, Mechanical and Aerospace Engineering. Earned Ph.D. based in part on work completed while employed on this project. Degree to be awarded May 2002. Thesis title: *Flame Suppression by Aqueous Compounds*. All degree requirements complete as of 2/7/02. Currently working as postdoctoral associate at Lawrence Livermore National Laboratory.

(5) Report of inventions

none

(6) References

Babushok, V.I., NIST, personal communication, 2001.

Glaude, P. A.; Curran, H. J.; Pitz, W. J.; Westbrook, C. K., *Proc. Combust. Inst.* 28: 1749-1756 (2000).

Lazzarini, A. K.; Krauss, R. H.; Chelliah, H. K.; Linteris, G. T., *Proc. Combust. Inst.* 28: 2939-2945 (2000).

Lott, J. L.; Christian, S. D.; Sliepcevich, C. M.; Tucker, E. E., *Fire Technology* 32: 260-271 (1996).

- Lutz, A. E.; Kee, R. J.; Grcar, J. F.; Rupley, F. M. "OPPDIF: A Fortran Program for Computing Opposed-Flow Diffusion Flames," Sandia National Laboratories, 1996.
- MacDonald, M. A.; Jayaweera, T. M.; Fisher, E. M.; Gouldin, F. C., *Combust. Flame* 116: 166-176 (1997).
- MacDonald, M. A.; Gouldin, F. C.; Fisher, E. M., *Combust. Flame* 124: 668-683 (2001).
- Papas, P.; Fleming, J. W.; Sheinson, R. S., *Proc. Combust. Inst.* 26: 1405-1412 (1997).
- Saso, Y.; Ogawa, Y.; Saito, N.; Wang, H., *Combust. Flame* 118: 489-499 (1999a).
- Saso, Y.; Saito, N., *Proceedings of the Proceedings of the 6th International Symposium on Fire Safety Science*, Poitiers, France, 1999b.
- Trees, D.; Seshadri, K.; Hamins, A. Experimental Studies of Diffusion Flame Extinction with Halogenated and Inert Fire Suppressants. In *Halon Replacements: Technology and Science*; Miziolek, A. W., Tsang, W., Eds.; American Chemical Society: Washington, DC, 1995; pp 190-203.
- Wainner, R. T., McNesby, K.L., Daniel, R.G., Miziolek, A.W., Babushok, V.I., *Proceedings of the 10th Halon Options Technical Working Conference*, Albuquerque, NM, 2000.